Catalysis of Hydrogen Azide Decomposition

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Summary Second and third row group VIII metals catalyse the decomposition of hydrogen azide to nitrogen and ammonium azide whereas iron, cobalt, and nickel react to form the respective nitrides which are inactive catalysts for HN_3 decomposition.

In a search for a low-temperature preparation of metal nitride catalysts, we have found that second and third row group VIII metals catalytically decompose hydrogen azide at 50—90 °C to yield nitrogen and ammonium azide. Surface sites of M–N–H composition appear to be intermediates in the catalysed decomposition.

Metal surfaces were prepared by vapour or solution deposition of a metal or a low-valent metal complex on η-alumina[1] followed by hydrogen reduction at 200 °C. Hydrogen azide diluted with helium was then passed over the metal-coated pellets. Iron, cobalt, and nickel reacted exothermally at *ca.* 100 °C to form the respective metal nitrides as indicated by *X*-ray and elemental analysis. All nitride phases present were not uniquely identified because the reaction conditions led to largely amorphous products. This chemistry provides the basis for a unique low-temperature synthesis of these nitrides. These nitrides were modest catalysts for ammonia synthesis from nitrogen and hydrogen at 300 °C and 1 atm. but none showed any activity as a catalyst for HN_3 decomposition from 100 to 250 °C. In contrast, the heavier metals of this group all initiated HN_3 decomposition within the temperature range 50—90 °C.

Conversions of hydrogen azide into nitrogen and ammonium azide were quantitative. Rhenium, but not molybdenum or tungsten, also exhibited this catalytic property. This difference may be accounted for by assuming that those metals that form nitrides simply react with the azide to give a nitride surface layer whereas those that do not form nitrides react with the azide, as discussed below, to generate continuously nitrogen and ammonium azide.

Homogeneous decomposition of $HN_3(g)$ begins at *ca.* 290 °C and initially follows the paths[2] in reactions (1)—(3).

$$HN_3 \rightleftharpoons NH + N_2 \qquad (1)$$

$$2NH \rightleftharpoons N_2H_2 \qquad (2)$$

$$2NH \rightleftharpoons N_2 + H_2 \qquad (3)$$

Ammonium azide is a common pyrolysis product that may arise from NH(g). Rice and Freamo[3] found that NH(g) condenses at -197 °C to a blue solid that forms NH_4N_3 on warming and also that NH(g) combines with H_2 and with CO to give NH_3 and HNCO, respectively. We find here that the catalytic reaction is sharply distinguished from the homogeneous decomposition. Catalytic decomposition of HN_3, in the presence of a large excess of D_2, yields ammonium azide that contains no deuterium. Addition of carbon monoxide to the reactant gas stream did not lead to detectable HNCO formation. Clearly, NH(g) is not formed in this catalytic decomposition. Furthermore it is unlikely that N–H bond cleavage of hydrogen azide is an important reaction pathway because the resultant M–H surface sites should be analogous to the M–D surface sites generated from $M + D_2$ (in the HN_3–D_2 reaction with the metal surface) and there should then be deuterium incorporation in the product, ammonium azide. Postulation of 'bound' N–H thus appears necessary to account for the experimental observations. A possibility is the interaction of the relatively nucleophilic nitrogen atom, vicinal to the hydrogen atom, with surface metal atoms to yield nitrogen and surface metal–N–H sites. Such nitrene surface complexes[4] of the form M–N–H or M–N(H)–M are expected to be intermediates, not simply transition states. As adjacent M–N–H sites develop, sequential or concerted switching of hydrogen from one nitrogen to another might provide the pathway to NH_3 (NH_4N_3) formation.

Metal transport was not observed in the catalytic reaction; hence molecules like $Os(NH)_4$ either were not formed or were not very stable under these conditions. Nevertheless, this chemistry suggests a synthetic possibility for nitrene (NH) complexes of transition metals as in the direct interaction of hydrogen azide and a co-ordinatively unsaturated complex. Preliminary studies of HN_3 reactions with 16-electron complexes like $[RhCl(PPh_3)_3]$ and $[Ni(PEt_3)_3]$ show primary formation of polyazido-metal derivatives; no NH_4N_3, metal nitrenes nor complexes that could be derived from metal nitrenes were detected. Ligand effects may be determinants in the reaction mechanism and these possibilities are being explored.

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[3] F. O. Rice and M. Freamo, *J. Amer. Chem. Soc.*, 1951, **73**, 5529.

[4] N–H metal complexes have not been isolated but have been postulated as intermediates (B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1972, **94**, 3786). An Ir–N–CF_3 complex has been described (M. J. McGlinchey and F. G. A. Stone, *Chem. Comm.*, 1970, 1265).